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**SUPPRESSION OF HIGH-SPEED C₂H₄/AIR FLAMES
WITH C₁-HALOCARBONS**

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Introduction

A shock wave preceding a turbulent flame can occur in a combustible mixture which is confined in space when the mixture composition falls within an appropriate range. Obstructions in the flow can promote the intense mixing of the fresh reactants with the combustion products and can cause pressure waves to interact with the mixing region. Given enough distance, the flame may accelerate dramatically, reaching a supersonic regime of flow. Depending upon the geometric details, the wave can approach its theoretical Chapman-Jouguet velocity and accompanying high pressure ratio. Even a slight variation in composition of the reactants near the limit of different combustion modes can cause a dramatic change in the wave velocity and destructive pressures to be attained.

An extensive literature describes the kinetics and dynamics of flame/shock wave systems formed within classical detonation tubes [*e.g.*, 1-4]. Chapman and Wheeler [5] noted as far back as 1926 that a methane/air flame could be accelerated to a terminal velocity in a shorter distance within a circular tube by placing obstacles into the flow. Lee, *et al.* [6], built on this observation to study quasi-detonations in hydrogen/air and hydrocarbon/air mixtures. A quasi-detonation propagates more slowly than a true detonation due to pressure losses in the flow, but its structure is more complex than a true detonation, and the mechanism of its propagation is not fully understood. Although an obstructed flow is more difficult to analyze than the flow in a smooth-walled tube, the former arrangement was chosen for the current study because it more closely simulates a potentially damaging condition which could occur should fuel leak into a confined space aboard an aircraft in the presence of an ignition source. The desire to rapidly suppress a flame and the associated pressure build up in such a situation is the primary motivation behind this study.

Halon 1301 (CF_3Br) has been used effectively onboard aircraft for a number of years to protect confined spaces called dry bays. However, new production of CF_3Br has ceased due to the deleterious role played by the bromine atom in stratospheric ozone destruction [7]. The work presented here is one

part of a comprehensive research program focused on the search for alternatives to CF_3Br for protecting aircraft in flight [8-9].

Experimental Facility and Operating Procedure

The effectiveness of a fire fighting agent in suppressing a high speed, premixed flame or quasi-detonation can be rated by the extent to which it decelerates the propagating wave and simultaneously attenuates the hazardous shock which is always ahead of the flame. Because the fire extinguishant is unlikely to be released prior to the establishment of a turbulent flame, the traditional experiment in which the flame inhibitor is premixed with the fuel and air prior to ignition does not replicate the chemistry critical to the actual situation. Each dry bay on an aircraft has a different geometry, and the release of the agent once a fire is detected is highly variable. The complexities and biases associated with the fluid dynamics of release can be avoided by premixing the agent with the fuel and air in a portion of the tube distinct from where the flame is initiated.

A two-section, deflagration/detonation tube has been designed to produce the desired environment for both the flame initiation and flame suppression regimes. A repeatable, uninhibited turbulent flame is fully established in the driver section, which is based directly upon the design of Peraldi, *et al.* [10].

Fig. 1 The driver section, shown to the left in Fig. 1, is 5 m long and is equipped at the closed end with a spark plug. This section was filled with the combustible mixture only. The ignition energy is delivered in a microexplosion of a tin droplet short-circuiting the tips of nichrome electrodes connected to an 80 V power supply. Spiral-shaped obstructions made of 6.4 mm stainless steel rods with a pitch equal to the inner diameter of the tube were inserted into the tube to produce an area blockage ratio of 44%, close to the value shown by Lee, *et al.* [6], to promote a quasi-detonation in their facility.

The second section of the deflagration/detonation tube contains the gaseous agent along with the same fuel/air mixture used in the driver section. The diameter is the same and its length is 2.5 m. An

identical spiral insert was used to maintain a high level of mixing. The two sections are separated from each other by a 50 mm inner diameter, stainless steel, high vacuum gate valve, which remains closed until just before ignition. Two pressure transducers and photodiodes are located 2.2 m beyond the gate valve and 0.3 m from the end of the tube. Their output was recorded on a multi-channel, digital, storage oscilloscope.

The whole system was evacuated to 10^{-1} Pa before filling the two sections separately with the desired mixtures, which were attained through the method of partial pressures. The fuel/air ratio and total pressures were held constant across the gate valve. The oxidizer used in all experiments was breathing grade air. Ethene (CP grade, 99.5% vol. purity) was chosen as the fuel because it has been demonstrated [10] that subsonic flames, quasi-detonations, and full detonations all can be obtained in a tube of this geometry simply by varying the stoichiometry. After filling, the gases were homogenized independently using a double, spark-free circulating pump, recirculating the entire tube volume a total of 20 times. The mixtures were left for five minutes to become quiescent. About ten seconds prior to ignition, the gate valve was opened manually.

After ignition, the flame propagates through the driver section and accelerates quickly due to the intense turbulence created by the interactions of the flow with the obstacles, generating a shock wave ahead of it. After passing through the open gate valve the flame/shock system encounters the same combustible mixture and a certain amount of agent in the test section. A rendering of the flame/shock system passing through the gate valve is shown in Fig. 2. Depending on the concentration of the agent, the flame may or may not be extinguished and the pressure wave attenuated.

A protocol was chosen [9] which minimized the impact of any of these parameters, and allowed flame/shock speeds to be obtained which were reproducible from run to run within $\pm 2\%$ (max. deviation). Pressure ratios downstream of the shock wave exhibited a higher variability, $\pm 20\%$ (max. deviation), because of the complex interactions between the spiral rod insert and the shock wave.

Experimental Results and Discussion

The experiments were conducted for equivalence ratios of 0.75 and 1.00, which corresponds to compositions by volume of 5.00% and 6.53% ethene, respectively, in the air plus ethene mixture. The initial reactant temperature was ambient (295 ± 3 K) and the initial total pressure was maintained constant at 100 ± 0.1 kPa.

Three dependent parameters were measured as a means to characterize the extent of flame suppression: Mach number, pressure ratio, and the distance separating the leading shock wave from the radiating flame. The Mach number was based upon the time it took for the pressure wave to travel the distance between the two pressure transducers, normalized by the sonic velocity of the reactant gases in the test section. The pressure ratio was evaluated from the average amplitude of the first pressure pulse to be recorded by each transducer, normalized by the initial pressure (100 kPa). In many cases, the first pressure pulse was less than the maximum measured. Consecutive pressure jumps occurred, possibly indicating that localized explosions in the mixing region between the spirals were present. (An individual experiment was concluded before the arrival of the shock wave reflected from the end plate.) The distance between the leading shock wave and the flame front was quantified by the time lag between the photodiode and pressure transducer response at the identical location.

Tab. 1

Table 1 summarizes the results with no suppressant in the test section, and compares the Mach number, pressure ratio, and flame spacing to the situation in a "fully suppressed" flame, in which pure nitrogen was located in the test section. Note that neither the Mach number nor pressure ratio go to zero for the fully suppressed case because total dissipation of the shock wave would require a substantially longer tube. On the other hand, the flame radiation disappears entirely; hence, the infinite separation distance.

The chemical compounds investigated in this study all contain a single carbon atom covalently bonded to four atoms chosen among fluorine, chlorine, bromine, iodine and hydrogen. Despite some

similarities in structure, the behavior of each chemical as it interacts with the shock wave and flame front was distinct.

Tetrafluoromethane, CF_4 The distance between the shock wave and flame front increases by more than an order-of-magnitude with as little as 2% (partial pressure) of CF_4 added to the test section.

Fig. 3

Figure 3 shows that the separation distance reaches a plateau at 60 mm for the stoichiometric flame. Decreasing the equivalence ratio to 0.75 increases this distance to 80 mm.

Fig. 4

The shock Mach number is plotted in Fig. 4 for all five compounds under lean conditions. A 2% partial pressure of CF_4 , plotted as ▼, reduces the Mach number from 3.4 to 2.4. Additional tetrafluoromethane further reduces the speed of the shock, until at 12%, the shock has been decelerated to about 1.4. When the fuel/air mixture is stoichiometric, the same behavior is observed; however, the value of the Mach number is uniformly higher across over the range of partial pressures examined.

The shock pressure ratio is affected by CF_4 in a manner similar to the Mach number. Under lean conditions, it decreases from its maximum value of 18 when no CF_4 is present to about 3 when a partial pressure fraction of 12% is added to the test section, as can be seen in Fig. 5 (▼ symbols). Experiments with stoichiometric ethene/air revealed nothing unexpected in the behavior of the pressure ratio. The value of P_1/P_0 was greater than that measured for lean combustion conditions, and it decreased monotonically with increasing CF_4 .

Fig. 5

Fig. 6

Trifluoromethane, CHF_3 The lone hydrogen on trifluoromethane reduces the suppression behavior of this compound. The distance between the flame and the shock wave is about half that of CF_4 when the mixture is stoichiometric. Figure 6 (open circles) shows that the flame begins to lag a substantial distance behind the shock only when the partial pressure fraction is increased to 10%. The difference in performance between CHF_3 and CF_4 is even more apparent when the lean mixture is used. A 7% partial pressure fraction of the non-hydrogenated compound leads to a flame separation distance four times that for the hydrogenated compound.

The Mach number is reduced very little when CHF_3 is added to the stoichiometric mixture, until the partial pressure exceeds 7% in the test section. The effect of small amounts of CHF_3 on the lean mixture Mach number is more apparent, as can be seen by the open-squares plotted in Fig. 4. As in the flame/shock separation distance, a plateau occurs between about 2% and 10%.

The open-squares plotted in Fig. 5 represent the pressure ratio in the lean CHF_3 experiments. This curve differs from the CF_4 not only in magnitude but also in slope. The trifluoromethane in concentrations below 10% (partial pressure) contributes enough hydrogen to the reactants that the shock pressure is substantially enhanced, reaching a maximum of 23:1 in 10% mixtures. An increase in shock pressure ratio does not occur under stoichiometric conditions, but the reduction in P_1/P_0 is modest when compared to the reduction caused by tetrafluoromethane at similar concentrations.

Chlorodifluoromethane, CHF_2Cl Replacing an additional fluorine with a chlorine atom further diminishes the agent's ability to suppress the high-speed flame. The shock Mach number (Fig. 4, open-triangles) is unaffected by the presence of up to 10% CHF_2Cl . Even when the test mixture contains 20% by partial pressure chlorodifluoromethane, the Mach number remains close to 2. The pressure ratio variation with the addition of CHF_2Cl is similar to what occurs when CHF_3 is added, up to about 10%. Both compounds lead to substantially higher pressure ratios than occur when no agent is added to the ethene/air mixture. For higher partial pressure fractions, the non-chlorine containing compound becomes significantly more effective.

Bromotrifluoromethane, CF_3Br The bromine atom in CF_3Br is known to inhibit laminar flames by scavenging hydrogen atoms from the chain-branching radical pool. At the lowest concentrations examined in the deflagration/detonation tube, CF_3Br is the most effective in reducing both the Mach number and pressure ratio across the shock wave. The results are plotted with solid circles in Fig. 4 and 5. Bromotrifluoromethane is also the most effective at higher concentrations, suppressing the flame at a partial pressure fraction of 10% to the same extent as if the test section were completely filled with

nitrogen. An unusual behavior occurs when the concentration is between 2% and 3%. Both the Mach number and pressure ratio increase with the amount of CF_3Br , followed by the expected decrease for large concentrations. The reversal, while small, is greater than the uncertainty in the data.

Iodotrifluoromethane, CF_3I The CF_3I in small concentrations is almost as effective as CF_3Br in attenuating the shock wave. The reversal which is slight with the bromine-containing compound becomes obvious with the iodide. The Mach number at a partial pressure fraction of 4% is 1.7, the lowest of all the agents examined. (See the open-circles in Fig. 4.) However, an increase in partial pressure to 6% increases the Mach number to 2.7, which is equal to or larger than the Mach numbers measured at that concentration for all the other agents except for CHF_2Cl . The reversal in performance is even more striking in Fig. 5, where the partial pressure ratio more than doubles as the level of CF_3I increases from 2% to 6%. At the latter concentration, the situation is made worse by the presence of the CF_3I than had no agent been added. A similar behavior was observed when iodotrifluoromethane was added to the stoichiometric ethene/air mixture.

Interpretation of Results The shock pressure ratio and Mach number yield qualitatively similar results. Effective suppression is accompanied by the reduction of both. The change in one as a function of concentration or equivalence ratio is generally mirrored in the other. An exception is the reduction in Mach number caused by intermediate levels of CHF_3 . It is clear that the hydrogen is contributing to the heat release behind the shock wave because the pressure ratio remains high. The mechanism by which this occurs at the same time the Mach number decreases is not revealed in the experiments.

Increasing the amount of tetrafluoromethane diminishes both the pressure and wave velocity in a manner which suggests the molecule is acting primarily as a thermal sink. This would be expected since CF_4 is known to be extremely stable. The C-H bond is weaker than the C-F bond, so that CHF_3 can thermally decompose to H and CF_3 . The hydrogen atom intensifies the combustion for moderate concentrations of CHF_3 , but eventually the inhibiting effect of the CF_3 kicks in. This can be observed

in the enhanced performance of CHF_3 under stoichiometric conditions, where the additional hydrogen-atom has less of a positive effect on the combustion.

Chlorodifluoromethane was observed to be relatively effective in suppressing atmospheric pressure, non-premixed flames in another portion of this research program [11]. However, it has also been observed to react violently with air under high pressure [12]. An intermediate behavior has occurred here; however, the complex reaction mechanism could not be expected to be revealed by the experiments performed.

The bromine- and iodine-carbon bonds are successively weaker than the C-F and C-Cl bonds. The non-monotonic behavior of both CF_3Br and CF_3I as their concentration was increased suggests competing reactions are present. One can speculate that the shock wave is sufficient to break the iodine bond before the flame arrives, setting up the iodine to scavenge the hydrogen atoms. The separation distance between the flame and shock wave in the CF_3I experiments was twice that measured in CF_4 . The iodine is more effective than the bromine at partial pressure fractions below 5% because it is likely to be present in higher concentrations. At higher partial pressures the iodine atom may combine to form I_2 , which does not interact with the combustion reaction. The fact that the CF_3I works counter to a suppressant in concentrations between 4 and 8% might be in agreement with the observation of Rollefson et al. [13] that iodine can enter into a catalytic cycle with an organic molecule to actually enhance the overall process.

Rating the Agents One objective of the research program was to develop a facility for rating the fire suppression capability of alternatives to CF_3Br . Table 2 ranks the five chemicals in three performance categories: amount required for total suppression (*i.e.*, flame radiation goes to zero, Mach number and pressure ratio approach 100% N_2 values), amount required to diminish the Mach number by 50% of maximum, and amount required for a 50% of maximum pressure reduction. In all three cases, the performance of CF_3Br under identical fuel/air conditions is used to normalize the results.

The relative values depend upon whether one chooses the mole fraction of the agent (which is assumed to be identical to the partial pressure fraction) or the mass fraction of the agent. On a molar basis, CF_3I is equal in performance to CF_3Br if one considers 100% suppression as the appropriate condition. Tetrafluoromethane is superior to all of the other chemicals, including CF_3Br , if one uses a 50% reduction in either the pressure ratio or Mach number as the appropriate criterion. Both the 50% pressure ratio and Mach number reduction approach yield a consistent ranking of agents, whether one uses a mole or mass basis. For the conditions covered in Table 2, the effectiveness of the agents on a mass basis, in decreasing order, is as follows: CF_4 , CF_3Br , CHF_3 , CF_3I , CHF_2Cl . The ranking is similar on a mole basis, except that trifluoromethane and trifluoroiodomethane exchange places. No experiments were run with CF_3Br under stoichiometric conditions, but the relative effectiveness of CHF_3 increased for an equivalence ratio of unity.

Conclusions

The experimental conditions in the deflagration/detonation tube facility differ significantly from those found in low-speed deflagration flames. The main qualitative difference is the occurrence of a strong shock wave ahead of the flame. That wave influences the gas dynamic, thermodynamic and chemical state of the pure combustible mixture in the driver section and the mixture containing an agent in the test section. Another feature is a high level of turbulence within the flame due to its high speed and the interactions with the spiral obstruction. The quantitative difference is a supersonic regime (relative to the undisturbed mixture) of flame/shock system propagation and strong pressure changes (due to confinement and shock) during the process. Thus the oxidizer, fuel and agent molecules undergo preliminary processes before entering the flame zone.

The following statements can be made based upon the results obtained:

1) Suppression of highly dynamic flames can be effectively studied in the two-sectional tube, permitting clear discrimination of performance among various extinguishing compounds.

2) The high-speed turbulent flame and the flame in the quasi-detonation wave under suppression strictly follows the shock wave which is always ahead of it in such a way that its velocity is the same as the shock velocity. The distance between the flame and the shock increases with the concentration of an extinguishing compound. At extinguishment the flame disappears while the residual shock still exists. The distance is dependent on the combustible mixture equivalence ratio and the chemical composition of an agent.

3) The most stable of the compounds, tetrafluoromethane, is the most effective in attenuating the pressure wave, decreasing the flame radiation, and reducing the flame speed. There is evidence of complex chemistry occurring following the arrival of the first shock and prior to the flame front in all of the partially substituted compounds.

4) The presence of hydrogen in the molecule increases the pressure ratio over a large concentration regime. The effect is exacerbated under lean conditions. The chlorine in CHF_2Cl further complicates the chemistry because it can act as an oxidizer and contribute to the exothermic process even under rich conditions.

5) Both the iodine and bromine appear to be released by the passage of the shock wave, and inhibit the flame effectively. The non-monotonic response of the pressure ratio to increasing the concentration of these compounds (especially CF_3I) suggests that there are competing reactions, with the Br and I either inhibiting or accelerating the combustion depending upon the concentration of the agent.

6) Other than CHF_2Cl , all of the C_1 -halocarbons investigated perform well in suppressing turbulent flames and/or quasi-detonations under the pressure, temperature, and fuel/air mixtures evaluated. The relatively poorer showing of CF_3I in the deflagration/detonation tube experiments, when

compared with suppression studies in constant pressure flames, is due to the different chemical kinetic pathways which dominate each system.

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Table 1. Summary of flame parameters for ethene/air mixtures under suppression extremes

Equivalence Ratio	Amount of N ₂ added to Test Section	Mach Number	Pressure Ratio	Flame/Shock Separation Distance, mm
0.75	0%	3.4 ± 0.1	18 ± 2	3 ± 1
0.75	100%	1.25 ± 0.05	2.5 ± 0.1	∞
1.00	0%	4.1 ± 0.1	26 ± 3	2 ± 1
1.00	100%	1.25 ± 0.05	2.5 ± 0.1	∞

Table 2. Performance of C₁-halocarbons relative to CF₃Br in suppressing high-speed flames

Suppressing Agent	Equivalence Ratio	100% suppression		50%, (M)		50%, (P ₁ /P ₀)	
		relative mass	relative moles	relative mass	relative moles	relative mass	relative moles
CF ₄	0.75	0.80	1.20	0.49	0.75	0.50	0.80
CHF ₃	0.75	0.82	1.50	1.41	3.00	1.20	2.70
CHF ₂ Cl	0.75	1.54	3.00	1.96	3.75	1.87	4.00
CF ₃ I	0.75	1.18	1.00	1.91	1.75	1.62	1.60

Figure Captions

- Fig. 1. Schematic of the deflagration/detonation tube facility.
DS - driver section, TS - test section, V - vacuum gate valve, CP - dual circulating pump, VP - vacuum pump, E - exhaust, IS - ignition source, F - fuel, O - oxidizer, A - agent, 1 - triggering transducer, 2,3 - piezo-electric dynamic pressure transducers, 4,5 - visible radiation fast photodiodes, SCOPE - collects two signals from pressure transducers plus two signals from photodiodes
- Fig. 2. Schematic of the flame/shock system propagation and suppression/attenuation processes.
1 - shock wave, 2 - turbulent flame, 3 - gate valve, 4 - driver section, 5 - spiral obstruction, 6 - test section
- Fig. 3. Effect of the C_2H_4 /Air mixture equivalence ratio in the presence of CF_4 on the flame-shock distance. Initial conditions: pressure, 100 kPa; temperature 295 K.
- Fig. 4. Suppression/attenuation effect of the C_1 -halocarbons based on the flame/shock Mach number in the lean 5% vol. C_2H_4 /Air mixture. Initial conditions: pressure, 100 kPa; temperature, 295 K.
- Fig. 5. Suppression/attenuation effect of the C_1 -halocarbons based on the shock pressure ratio in the lean 5% vol. C_2H_4 /Air mixture. Initial conditions: pressure, 100 kPa; temperature, 295 K.
- Fig. 6. Effect of the C_2H_4 /Air mixture equivalence ratio in the presence of CHF_3 on the flame-shock distance. Initial conditions: pressure, 100 kPa; temperature 295 K.











